Measurements on the Gases Evolved from Glasses of Known Chemical Composition

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SYNOPSIS: This paper has a very direct bearing upon the pumping or exhausting of the vacuum tubes used in telephone repeaters and similar thermionic tubes. The telephone repeater bulb, as is well known, holds a vacuum of the order of 10^{-6} mm. of mercury. In order to produce this vacuum it is necessary during the manufacture of the tube to not only remove the air from the space within the bulb but also to allow very considerable amounts of various gases to diffuse out from within the glass of the bulb and the metal parts of the tube structure. The volume of gas which is frequently removed from the metal plates, for instance, may be roughly estimated as 100 times the volume of the plates themselves, the volume of the gas being measured at atmospheric pressure. To remove these gases from the bulb and metal parts, it is necessary to maintain during the pumping process a temperature which is far above the normal temperature and a fair degree of vacuum within the bulb for a period of time which varies from a few minutes to an hour or more depending upon the type of tube.

With a view to simplifying the pumping process, the authors have found that a glass relatively free from absorbed gases can be produced by using special precautions in manufacture. The authors have also measured and analyzed the gases evolved from glasses of various composition. Seven different samples representing four distinct types of glass have been experimented with. Six of these samples of glass have been carefully analyzed and definite relations found between the amounts and kinds of gases evolved and the chemical composition of the glasses.—*Editor.*

THIS investigation of the gases evolved by certain glasses when heated was undertaken with a view to securing a glass which, after an initial period of heating, should cease to give off appreciable quantities of gas. The use of such a gas-free glass would obviously be desirable in the experimental investigation of vacuum tubes, in which the filament and other parts within the tube may be affected adversely by gases evolved from the heated glass during manufacture of the tube.

The work of Guichard (11), Langmuir (19), Sherwood (30), Washburn (37), and others has established the following points with respect to the gases evolved by the glass when heated. The gases may be held as an adsorbed film or dissolved throughout the glass; the adsorbed gases are evolved readily at temperatures less than 300°C., whereas the dissolved gas, although it begins to come out of the surface layers at 200°C., comes out slowly, by reasons of the slowness of diffusion through the glass, even at much higher temperatures. Consequently the total gas evolved at each of a series of temperatures is a maximum somewhere between 200°C. and 400°C.; this decreases to a minimum, and rises again at temperatures approaching the softening range of the glass.

The main gases held by the glass are carbon dioxide (from the carbonates and possibly from the furnace gases), water (from the materials and the furnace gases), with smaller quantities of sulphur dioxide, oxygen and nitrogen. The amounts of the gases may correspond to a real equilibrium under the condition of melting; but more usually the viscosity of the melt has been such as to prevent the gases present in solution from escaping completely during the melting period. Commerical glasses consequently retain some gas which escapes slowly when the glass is reheated.

In most of the investigations published in the past the gases have been divided into three fractions: (a) condensable above –78°C. (b) condensable between –78°C. and –190°C., (c) not condensable at –190°C. These fractions represent with fair accuracy (a) water vapor, (b) carbon dioxide, (c) the permanent gases; oxygen, nitrogen, hydrogen. In general water vapor is the most abundant, followed by carbon dioxide; but, owing to lack of the necessary data, it is not possible to correlate these findings with the composition of the glass, still less with the mode of its melting.

Apparatus and Method

The apparatus used for determining the gases evolved from the glass on being heated is shown in Fig. 1.

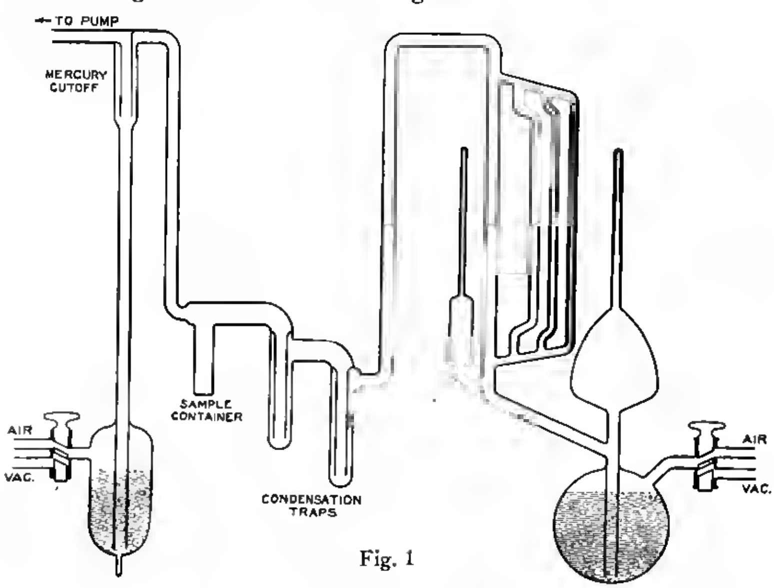

Fig. 1

The water vapor was removed by surrounding the condensation trap by a mixture of frozen and liquid acetone contained in a Dewar

vessel; this mixture being obtained by adding liquid air to acetone until its freezing point −95°C. was reached. The carbon dioxide was removed similarly by means of liquid air. Readings were taken on the McLeod gauge (1) with no condensing agent, this giving the pressure of the total gas evolved; (2) with frozen acetone as condensing agent, this giving the pressure of gases less the water vapor, and (3) with liquid air as condensing material, corresponding to the pressure of the permanent gases. From the several pressures thus obtained the respective volumes could readily be calculated.

For the purpose of determining the amount of gases given up by the various types of glass, the glass was first cleaned with chromic acid, and washed thoroughly with water. It was then placed in the sample container (made of the same glass as that being tested) and the pump operated for several hours in order to dry the sample thoroughly. The pump used (a mercury vapor pump in conjunction with two oil pumps) was operated until the pressure within the apparatus after being trapped off from the pump remained constant at about 1×10^{-6} mm. for a period of at least two hours. The glass was then heated to a temperature as close to the softening range as it was possible to go without causing the container to collapse; it was kept at this temperature until the gas pressure became constant, when the volumes of the gases were determined in the manner outlined above. The period required for completely driving off the gases ranged from sixty-five to eighty hours.

Types of Glass Used

The types of glass worked with, together with their chemical compositions are given in Table I.

TABLE I.

Chemical Analysis of the Glasses Used

	1	2	3	4	5	6
SiO_2	69.93	69.40	64.64	61.50	72.05	65.47
Al_2O_3	1.54	.78	.20	.57	2.21	2.99
Fe_2O_3	.19	.14	.04	.11	.05	.51
PbO	1.44	Trace	21.66	22.55	6.11	20.20
CaO	3.17	5.15	.02	.21	.06	.22
MgO	.03	4.09	.02	.36	.09	.13
Na_2O	21.02	16.67	9.10	8.14	4.23	6.40
K_2O	.10	.20	3.20	3.76	1.12	3.59
P_2O_5	.08	.16	.75	.34	Trace	Trace
Sb_2O_3	.05	.10	....	....	Trace	....
MnO_2	.09	.19	....	.19	.01	.073
F_2	....	....	Trace	....	Trace	....
B_2O_3	2.36*	3.12*	.37*	2.27*	14.07*	....
SO_3	....	....	....	....	....	.013
BaO	....	....	....	....	....	Trace

* By difference.

It will be observed that glasses No. 1 and No. 2 are soda-lime glasses; 3, 4 and 6 are soda-lead glasses; 5 is a boro-silicate of lead and soda.

Experimental Results

The results of the determinations are shown in Table II.

TABLE II.

Gases Evolved from Glass of Known Chemical Composition During Heat Treatment in Vacuo

I	II	III	IV	V	VI		VII	VIII	IX
No. of Sample	% Alkali in the Glass	Vol. of Sample cc	Surface Area Cm^2	Temp. to which Glass Was Heated °C.	Total Gas Vol. cc		Comp. of Gas %	Vol. in cc Per Cm^2 x 10^4	Vol. Per cc Glass x 10^4
1	21.12	37.2	580	400	H_2O	2.70	88.5	46.6	726
					CO_2	.32	10.5	5.5	86
					P.G.	.03	1.0	.5	8
						3.05		52.6	820
2	16.87	31.9	540	400	H_2O	1.62	92.6	30.0	508
					CO_2	.11	6.3	2.0	34
					P.G.	.02	1.1	.4	6
						1.75		32.4	548
3	12.30	26.5	565	400	H_2O	1.34	96.4	23.7	506
					CO_2	.03	2.2	.5	11
					P.G.	.02	1.4	.4	8
						1.39		24.6	525
4	11.90	24.1	540	400	H_2O	1.37	97.2	25.4	568
					CO_2	.02	1.4	.4	8
					P.G.	.02	1.4	.4	8
						1.41		26.2	584
5	5.35	25.2	469	500	H_2O	.03	33.3	.6	12
					CO_2	.04	44.5	.9	16
					P.G.	.02	22.2	.4	8
						.09		1.9	36
6	9.99	15.6	292	400	H_2O	.03	49.6	1.0	19.
					CO_2	.03	49.6	1.0	19.
					P.G.	.0005	.8	.02	.3
						.0605		2.02	38.3

* P.G. = Permanent Gases.

If we may assume that the low melting glasses (1-4) worked with in this investigation received approximately the same heat treatment during their manufacture, then the data presented in Table II would indicate that there is a definite relation between gas evolved and the chemical composition of the glass. The amount of gas given up per square centimeter of glass surface is found to be closely parallel to the alkali content except in the case of glass number 6. This parallelism holds more closely for the amount of water vapor than it does for the other gases, although the relation does hold to a less striking extent for carbon dioxide. In a paper by Niggli (24), that treats of the phenomena of equilibrium between R_2O, $Si\ O_2$ and CO_2 ($R_2O = Na_2O, K_2O, Li_2O$), in melts at temperatures of 900 to 1000°C. under a pressure of one atmosphere CO_2, it is interesting to note, that the results obtained show the amount of CO_2 in the melt, when equilibrium is reached, to decrease as the composition of the melt becomes less alkaline. The amount of permanent gases evolved is roughly the same for the various types of glass. The reason for glass number 6 falling out of line with the other glasses will be discussed later. The authors, after making inquiries at several glass manufacturing concerns, feel that the statement can be made with a fair degree of justice that ordinary commercial glasses of like composition usually receive approximately the same heat treatment in their manufacture. Preservation of melting pots, saving in fuel, etc., make it very essential for the glass manufacturer to know the lowest temperature that can be used with the assurance of producing good glass. In all the glass factories where we made inquiries we found that this minimum temperature was about constant in cases where glasses having about the same melting points were being made. In these factories we were also told that the furnaces were usually held as near this minimum temperature as possible throughout the entire melting process.

Glass number 5 undoubtedly received a higher heat treatment in the melting process, because of its higher melting point and greater viscosity, than did the other glasses that were tested. The data given in Table II shows that this glass gave off very little gas when subjected to heat treatment in vacuo. The high heat treatment that this glass received in its manufacture is probably responsible in part for this small evolution of gas, but its low alkali content is probably equally responsible. It will be noted when reference is made to Table II that this glass was heated to 500°C. whereas the other glasses were only subjected to a heat treatment of 400°C.

Evolution of Adsorbed and Absorbed Gas

To determine the relations of adsorbed gases to absorbed gases in the six samples of glass, the pressures of the gases evolved were determined at intervals of 100°C. from 100°C. to the softening point of the glass. In addition to the six samples of glass, a run was taken on

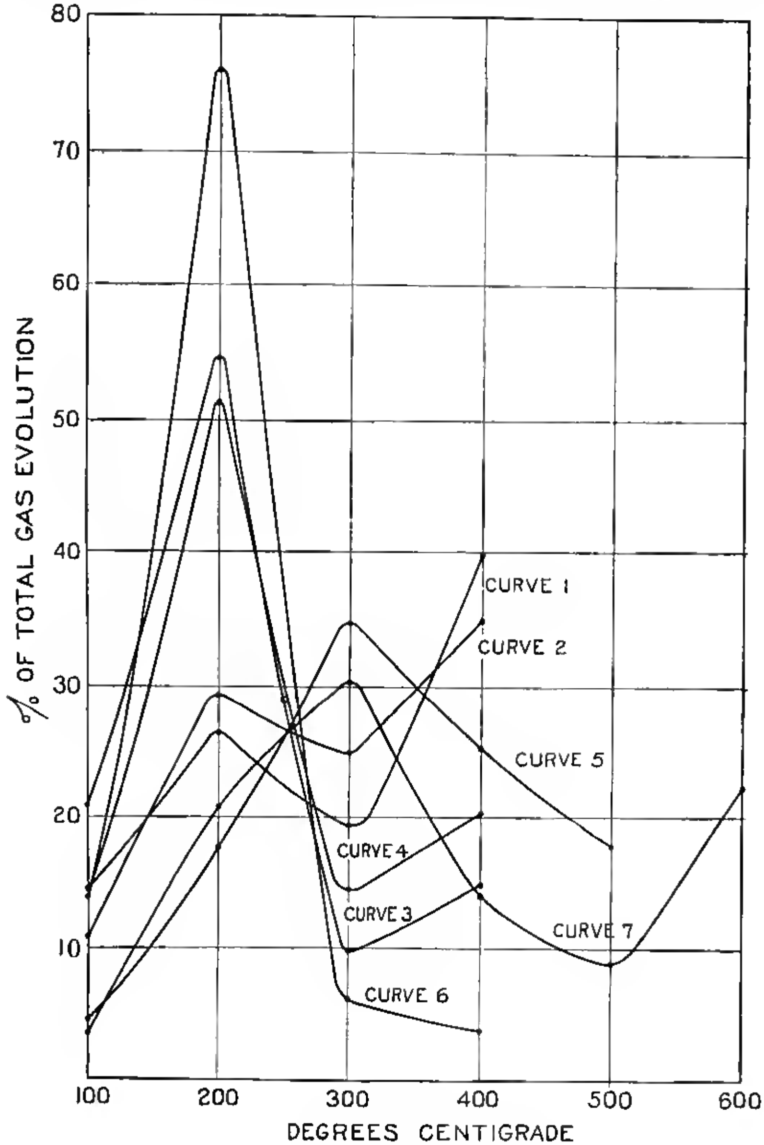

Fig. 2

a Pyrex Glass which will be indicated in the experiment as number 7. No analysis was made of this glass but it is known to be a boro-silicate glass practically free from alkali and heavy metals. From the pressures of the gases obtained, the distribution of gas evolution over the various intervals was determined. Expressed in terms of percentage of the total gas evolved over the entire range, these results are shown graphically in Fig. II.

It will be noted first of all that these curves with the exception of number 6, are in general similar to those obtained by Sherwood (loc. cit.) in that they show both maximum and minimum points. Glass No. 6 was found in this experiment as in the preceding one to behave quite differently from numbers 3 and 4, although chemically it is very similar. The explanation for this difference will appear later. The curves show very clearly the distinction between the adsorbed and absorbed gases. It is seen that the adsorbed gases for the lime and lead glasses are practically all given up at a temperature of 200°C. while 300°C. is required in the cases of the boro-silicate glasses. The absorbed gases begin to come off at the softening points of the various glasses; 400°C. for the lead and lime glasses and 600°C. for the boro-silicate glasses. The steeper slopes of the curves 1 and 2 above 300°, as compared to 3 and 4 are undoubtedly due to the fact that these glasses (lime glasses) become fluid more rapidly than do the lead glasses and therefore give up their dissolved gases at a more rapidly increasing rate than do the others. In this connection it should be stated that the amount of absorbed gases found in the above experiments represent only that portion of the dissolved gases which lie nearest the surface of the glass. Owing to the great viscosity of the glass at the temperatures used, the rate of diffusion of the gas would be altogether too slow to permit any considerable portion to reach the surface.

Some data that were taken in some of the experiments carried on in the investigation of the adsorbed gases are interesting in that they seem to throw considerable light on the question of the manner in which these gases are held to glass. Warburg and Ihmori (36) have maintained that the gases are held by chemical forces (primary valence forces) while other writers have maintained that the gases are held primarily by physical forces (secondary valence forces). The measurements of Warburg and Ihmori were made with water vapor and while no analyses of the glasses were made, it was found that only those glasses that contain alkali were capable of taking up water vapor.

Glasses Nos. 1, 2, 3, 4, 5 and 6 were experimented with in this connection. The glasses were heated to a temperature high enough to

drive off all the adsorbed gases as indicated by the curves in Fig. 1 (200° for Nos. 1, 2, 3 and 4 and 300° for No. 5.) and the amount of carbon dioxide and permanent gases determined. The results are shown in Table III.

TABLE III.

Showing the Relation Existing Between Adsorbed Carbon Dioxide and Percentage Alkali in the Glass

Glass No.	Vol. of Adsorbed CO_2 in cm^3 x 10^5 per cm^2	Vol. of Adsorbed Permanent Gas in cm^3 x 10^5 per cm^2	% Na_2O+K_2O in Glass
1	19.3	1.30	21.12
2	10.4	1.80	16.87
3	7.5	2.65	12.30
4	7.5	2.35	11.90
5	4.5	.48	5.35
6	6.5	.009	9.99

These data show in a remarkable way the relation existing between the adsorbed carbon dioxide and the alkali content of the glass. This experiment would seem to indicate that adsorbed carbon dioxide is held by primary valence forces. Many other glasses must be tested, however, before such a statement can be accepted as a fact. It seems very plausible, however, to believe that carbon dioxide is taken up by a film of sodium hydroxide which has been formed by the slow hydrolysis of the glass.

This coincides with the view of Kraus (17) who found, in the case of a single glass which was high in soda, that no carbon dioxide was adsorbed when glass and gas were both carefully dried and also that on carbon dioxide is adsorbed by the glass if it has been washed with boiling water to remove the film of alkali on the surface. The above results do not necessarily indicate, however, that all gas held on the surface of the glass is held by primary valence forces. Indeed a determination that was made of the permanent gases given up by the glass up to 200°C. would indicate that these gases are held to the glass primarily by secondary valence forces. Table III shows that while appreciable quantities of these gases were evolved, no correlation existed between these quantities and the chemical composition of the glass. A similar determination was not made for water vapor because the capacity of the McLeod gauge used in the experiment was too small to take care of the large quantities of water vapor evolved; if a determination had been made in this connection, it seems highly probable that a definite relationship, existing between the adsorbed water vapor and the alkali content of the glass, would have been noted.

Manufacture of Relatively Gas Free Glass

In our first experiment we melted some ordinary commercial glass in vacuo. The temperature within the vacuum furnace was kept considerably above the melting point of the glass under examination and was held there for a period of about one hour. For a portion of this time huge quantities of gas were evolved. After this evolution subsided the furnace was cooled to room temperature and the melt was removed. Some of the glass obtained from this melt was later reheated in vacuo at various temperatures up to 500°C. At the lower temperatures from 20°C. to 200°C. a measurable amount of gas was evolved, but above 200°C. there was practically no gaseous evolotion. The results obtained from this and other similarly conducted experiments make it seem probable that a vacuum furnace process for the manufacture of certain kinds of glass is possible. The expense incurred, however, in the manufacture of gas free glass by this method would undoubtedly always prohibit its general use in the industries. After realizing that owing to the difficulties of making it, a gas free glass could be used only in a very limited field, we sought next to determine if it would not be possible to modify the ordinary standard procedure now pursued in glass making in such a way as to make a relatively gas free glass.

At our request, the Corning Glass Works agreed to undertake some experiments to produce glass that would be more nearly gas-free than that obtainable on the market.

In one of the most successful experiments and the only one that will be recorded here, materials that would produce a low melting point glass were subjected to a heat treatment of between 1500°C. and 1600°C. for a period of one hour. For a chemical analysis of the glass produced and for its behavior upon being heated in vacuo see Tables I and II—Glass 6.

Attention has been called to the fact that this glass behaved quite differently in the above experiments from the other glasses of the same type in two particulars (1) the total amount of gas given up by the glass is very much less than for the other glasses of like composition and (2) of the gas given up by this glass, 90% is given up at 200°C. indicating that this proportion of the gas is adsorbed gas. We may conclude then that the special treatment of this glass in its manufacture was very efficient in so far as the removal of the absorbed or dissolved gas was concerned. It could not, however, prevent the adsorption of gases by the glass on standing. The adsorbed gases, however, are rather unimportant from the standpoint of vacuum

tube work since such gases can be fairly readily removed by a preliminary heating.

Summary of Results

The results of our investigation may be summarized as follows:

(1) Glasses whose compositions run high in alkali give off more gas during their heat treatment than do those of lower alkali content.

(2) A definite relation appears to exist between the amount of water vapor held by a glass and its alkali content.

(3) A relation, although not as pronounced as that mentioned above, appears to exist between the amount of carbon dioxide held by a glass and its alkali content.

(4) Adsorbed carbon dioxide seems to be held to glass primarily by primary valence forces.

(5) Adsorbed permanent gases seem to be held to glass primarily by secondary valence forces.

(6) Glass relatively free from absorbed gas can be produced by means of heating the glass during its melting process to a sufficiently high temperature.

In conclusion the authors wish to express their thanks to Dr. J. Johnston to whom they are especially indebted for assistance and advice.

BIBLIOGRAPHY

(1) Allen, E. T. & Zies, E. G. J. Am. Coram. Soc. *1* 739–790, 1918.
(2) Briggs, H. Nature, *107*, 285–286, 1921.
(3) Bunsen, R., Ueber die Verdichtung der CO_2 an blanken Glasflächen. Ann. d. Phys. (3) *20*[1], 545–560, 1883.
(4) ———Ueber die langsame Verdichtung der CO_2 an blanken Glasflächen und Kayser's Einwürfe dagegen (3), *22*, 145–152, 1884.
(5) ———Ueber capillare Gasabsorption. Ann. d. Phys. (3) *24*, 321–347, 1885.
Campbell, N. R. See Research Staff of G. E. Co.
(6) Campbell Swinton, A. A. The occlusion of the residual gas by the glass walls of vacuum tubes. Proc. Roy. Soc. A79, 134–137, 1907.
(7) ———The occlusion of the residual gas and the fluorescence of the glass walls of cathode tubes. Proc. Roy. Soc. *A81*, 453–59, 1908.
(8) Chappius, P., Die Verdichtung der Gase auf Glasoberflächen, Ann. d. Phys. (3) *8*, 1–29, 1879.
(9) Giesen, J. Einige Versuche mit der Salvionischen Mikrowage. Ann. d. Phys. (4) *10*, 830–844, 1903.
(10) Gouy, Sur la penetration des gaz dans les parois de verre des tubes de Crookes. C. R. 122, 775–76, 1896.
(11) Guichard, Sur les gaz degages des parois des tubes de verre. Bull. Soc. Chim. Paris, (4) *9*, 438–42, 1911.
(12) Hill, S. E. The absorption of gas in vacuum tubes. Proc. Phys. Soc. London, *25*, 35–43, 1912.

(13) Hughes, A. Ll. Dissociation of hydrogen and nitrogen by electron Impacts. Phil. Mag. (6) *41*, 778–798, 1921.
(14) Ihmori, T. Ann. Physik (3) *31*, 1006–1014, 1889.
(15) Jamin, L. and Bertrand, A. Note sur la condensation des gaz a la surface des corps solides. C. R. *36*, 994–98, 1853.
(16) Kayser, H. Ueber die langsame Verdichtung der CO_2 an blanken Glasflächen Ann. d. Phys. (3) 21, 495–498, 1884.
(17) Krause, H. Ueber Adsorption and Condensation. *V.* CO_2 an blanken Glasflächen. Ann. d. Phys. (3) 36, 923–36, 1889.
(18) Langmuir, I. Tungsten lamps of high efficiency. A. I. E. E. Trans. *32*, 1913–33, 1913.
(19) Langmuir, I. Adsorption of gases on plane surfaces of glass, mica, and platinum. J. Am. Chem. Sec. *40*, 1361–1403, 1918.
(20) Magnus, G. Ueber die Verdichtung der Gase an d. Oberfläche glatter Körper. Ann. d. Phys. (2) *89*, 604–10, 1853.
(21) Mehlhorn, F. Ueber die von feuchten Glasoberflächen fixirten permanenten Gase, Verh. d. deutsch. Phys. Ges. *17*, 123–28, 1898.
(22) Menzies, A. W. C. J. Am Chem. Soc. *42*, 978, 1920.
(23) Mulfärth, P. Adsorption of Gases by Glass Powder. Ann. d. Phys. (4), *3*, 328–52, 1900. Sci. Abs. 4, I 162, 1901.
(24) Niggli, P. The Phenomena of Equilibria Between Silica and the Alkali Carbonates, J. Am. Chem. Soc. *35*, 1693–1727, 1913.
(25) Parks, J. Thickness of the liquid film formed by condensation at the surface of a solid. Phil. Mag. (6) *5*, 517–523, 1903.
(26) Pettijohn, J. Am. Chem. Soc. *4*, 477–486, 1919.
(27) Pohl, R. Die Bildung von Gasblasen in den Wändenerhitzter Entladungsröhre. Verh. d. deutsch, Phys. Ges. *5*, 306–314, 1907.
(28) Research Staff of G. E. Co., London. The disappearance of gas in the electric discharge. Part 1. Phil. Mag. (6) *40*, 585–611, 1920.
(29) ——————Part II. Phil. Mag. (6) *41*, 685–706, 1921.
(30) Sherwood, R. G. Effects of heat on chemical glassware. J. Am. Chem. Soc., *40*, 1645–53, 1918.
(31) Sherwood, R. G. Gases and vapors from glass. Phys. Rev. (2) *12*, 448–458, 1918.
(32) Shrader, J. E. Residual gases and vapors in highly exhausted glass bulbs. Phys. Rev. (2) *13*, 434–437, 1919.
(33) Soddy, F. and Mackenzie, T. D. The electric discharge in monatomic gases. Proc. Roy. Soc. *A80*, 92–109, 1907.
(34) Ulrey, D. Evolution and absorption of gases by glass. Phys. Rev. (2) *14*, 160–161, 1919.
(35) Vegard, L. On the electric discharge through HCl, HBr, HI, Phil. Mag. (6), *18*, 465–483, 1909.
(36) Warburg, E. and Ihmori, T. Ueber das Gewicht and die Ursache der Wasserhaut bei Glas and anderen Körpern. Ann. d. Phys. (3), *27*, 481–507, 1886.
(37) Washburn, E. W. Dissolved Gases in Glass. Univ. of Ill. Bulletin No. 118.
(38) Willows, R. S. On the absorption of gases in a Crookes tube. Phil. Mag. (6) *1*, 503–517, 1901.
(39) Willows, R. S. and George, H. T. The absorption of gas by quartz vacuum tubes. Proc. Phys. Soc. London, *28*, 124–131, 1916.